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(54) Corrosion Inhibition

(57) A method of inhibiting corrosion of a non-ferrous metal body in a water system, such as a condenser being supplied with cooling water, comprises adding to the water a solution of a mixture of ferrous

sulphate and an organic polymeric material, in sufficient quantity to deposit an even layer of ferric hydroxide on the non-ferrous metal body. The mixture preferably includes a reducing or chelating agent. An admixture for use in the method is claimed.

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# **SPECIFICATION** **Corrosion Inhibition**

The invention relates to corrosion inhibition, and particularly to the inhibition of corrosion of a non-ferrous metal body in a water system such as a cooling system which uses water as a coolant.

Water is often used as a coolant in industrial, domestic and other cooling systems. In most cases such systems have parts, for example a condenser, made of non-ferrous metal such as aluminium, brass or cupro-nickel or like alloys. These metals, although less susceptible to corrosion than some metals, may corrode where they are in contact with the cooling water, and failure of a condenser may involve costly closure of the system whilst the necessary repairs are effected. We have found that this corrosion can be overcome or at least substantially reduced, by providing an even layer of ferric hydroxide on the surface of the non-ferrous metal parts, which come into contact with the cooling water. The invention may be applicable to any water system which has non-ferrous metal parts in contact with water.

According to the invention there is provided a method of inhibiting corrosion of a non-ferrous metal body in a water system, comprising adding to the water of the system a solution of a mixture of ferrous sulphate and an organic polymeric material, in sufficient quantity to deposit an even layer of ferric hydroxide on the non-ferrous metal body.

Whilst the mechanism by which the invention works is not fully understood, we have determined that if a solution of ferrous sulphate alone is used, the ferric hydroxide is not deposited in an even layer and some areas of the metal body are still susceptible to corrosion. On the other hand, the use of a solution of the organic polymeric material alone has little or no effect in inhibiting corrosion.

The mixture preferably contains from 60% to 99% ferrous sulphate, and from 1% to 40% organic polymer, by weight, to ensure that the ferric hydroxide is deposited in an even layer.

The preferred organic polymeric material comprises one or more of cellulose ethers or substituted cellulose ethers; naturally occurring starches such as potato, maize or tapioca starches; naturally occurring gums such as guar; polysaccharides or substituted polysaccharides such as glycogen, inulin and substituted inulin; and synthetic organic polymers such as polyacrylamides, substituted polyacrylamides, polyamides, polyimines, polyamines, polyethyleneglycol, polyvinyl acetate, polyvinyl pyridine, polyacrylic acid and derivatives of polyacrylic acid.

The mixture preferably includes a reducing agent for ferric ions. Examples of suitable reducing agents are stannous chloride, tartaric acid, ascorbic acid and glucose or reducing sugars. The inclusion of the reducing agent has been found to produce a surprising increase in the

effectiveness of the solution in inhibiting corrosion, and probably acts in the additive solution to hold the ferrous ions in the reduced state, while producing little or no effect when diluted in the water of the system. For best effect the reducing agent is preferably 10% or less of the mixture, and most preferably from 0.1% to 5% of the mixture, by weight.

Alternatively, the mixture may include a chelating agent for ferric or ferrous ions in the same preferred ranges as for the reducing agent. Suitable chelating agents are ethylene diamino tetra acetic acid (EDTA), heptonates, phosphonic acid derivatives and alkanolamines among others.

The mixture will normally be supplied as a free flowing powder with the ferrous sulphate present as the hydrated compound having the formula  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The mixture preferably includes a flow assisting agent for the mixture. The flow assisting agent may be any one or more of calcium and magnesium silicate, precipitated silicas, and a mixture of calcium carbonate and calcium stearate. The solution is preferably added to the water of the system to give a mixture dosage of from 0.05 to 100 parts per million by weight, and more preferably from 0.1 to 50 parts per million by weight. If the dosage is too low, say below 0.05 parts per million, the effectiveness of the solution in inhibiting corrosion is reduced, and if the dosage is too high, say above 100 parts per million, the method becomes expensive and no further improvement in corrosion inhibition is achieved.

especially effective dosage is achieved between 0.2 and 2.5 parts per million by weight, since the tendency of ferrous ions to change to ferric ions in the water of the system is greatest within this range. On the other hand it is necessary to maintain the relatively concentrated additive solution in the ferrous state before dilution in the water system, which may be achieved by the use of the reducing or chelating agents.

The invention includes an admixture as described above, for use in the method of the invention.

The following examples serve to illustrate the composition of corrosion inhibitor admixture according to the invention:

## **Example 1**

|     |   |     |
|-----|---|-----|
| ... | Ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ )  | 80% |
|     | Sodium hydroxyethyl methyl cellulose (molecular weight 150 000) | 18% |
| 115 | Sodium heptonate (chelating agent)                              | 2%  |

## **Example 2**

|     |  |     |
|-----|--|-----|
|     | Ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) | 95% |
| 120 | Modified Potato Starch (anionic)                               | 4%  |
|     | Ascorbic acid (reducing agent)                                 | 1%  |

## **Example 3**

|     |  |      |
|-----|--|------|
|     | Ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ )   | 98%  |
|     | Polyacrylamide (cationic; molecular weight 1 000 000)            | 1.5% |
| 125 | 1-Hydroxyethylidene and 1,1-Diphosphonic acid (chelating agents) | 0.5% |

**Example 4**

|  |     |
|--|-----|
| Ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) | 88% |
| Sodium carboxymethyl cellulose<br>(molecular weight 50 000)    | 7%  |
| Guar gum   | 3%  |
| EDTA   | 1%  |
| Stannous chloride (reducing<br>agent)                          | 1%  |

**Example 5**

|  |      |
|--|------|
| Ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ )   | 90%  |
| Sodium carboxymethyl cellulose<br>(molecular weight 50,000)      | 7%   |
| Sodium heptonate (chelating<br>agent)                            | 2.5% |
| Calcium carbonate and calcium<br>stearate (flow assisting agent) | 0.5% |

The mixture of each example was mixed with water to give an additive solution of between 0.1% and 10% wt/vol. Each solution was added to the cooling water of a steam generating plant in which the cooling water circulated through a non-ferrous metal condenser to re-condense steam for re-use as a boiler feed.

In each case the additive was found to be effective in inhibiting corrosion of the condenser, by depositing an even layer of ferric hydroxide on the surface of the condenser in contact with the cooling water. A substantial increase in the working life of the condenser was obtained.

1. A method of inhibiting corrosion of a non-ferrous metal body in a water system, comprising adding to the water of the system a solution of a mixture of ferrous sulphate and an organic polymeric material, in sufficient quantity to deposit an even layer of ferric hydroxide on the non-ferrous metal body.

2. A method according to Claim 1, in which the mixture contains from 60% to 99% ferrous sulphate, and from 1% to 40% organic polymer, by weight.

3. A method according to Claim 1 or 2, in which the organic polymeric material is one or more of cellulose ethers or substituted cellulose ethers, naturally occurring starches, naturally occurring gums, polysaccharides or substituted

polysaccharides, and synthetic organic polymers.

4. A method according to any preceding claim, in which the mixture includes a reducing agent for ferric ions.

5. A method according to Claim 4, in which the reducing agent is 10% or less of the mixture, by weight.

6. A method according to Claim 5, in which the reducing agent is from 0.1% to 5% of the mixture, by weight.

7. A method according to any one of Claims 1 to 3, in which the mixture includes a chelating agent for ferric or ferrous ions.

8. A method according to Claim 7, in which the chelating agent is 10% or less of the mixture, by weight.

9. A method according to Claim 8, in which the chelating agent is from 0.1% to 5% of the mixture, by weight.

10. A method according to any preceding claim, in which the solution is added to the water of the system to give a mixture dosage of from 0.05 to 100 parts per million by weight.

11. A method according to Claim 10, in which the mixture dosage is from 0.1 to 50 parts per million by weight.

12. A method according to Claim 11, in which the mixture dosage is from 0.2 to 25 parts per million by weight.

13. A method according to any one of Claims 1 to 12, in which the mixture is used for the corrosion of a non-ferrous metal body in a water system, the mixture being added to the water system in the form of a solution.

14. A mixture for use in the method of any one of Claims 1 to 13, which comprises ferrous sulphate, an organic polymeric material or a reducing agent for ferric ions or a chelating agent for ferric or ferrous ions.

15. A mixture according to Claim 14, which includes a flow assisting agent for the mixture.

16. A mixture according to Claim 15, in which the flow assisting agent is any one or more of calcium and magnesium silicate, precipitated silicas, and a mixture of calcium carbonate and calcium stearate.

17. A mixture for use in inhibiting corrosion of a non-ferrous metal body in a water system, which is substantially as described in any one of the Examples.